

Temperature Swing Adsorption of Uranium (VI) ions on Poly(*N*-isopropylacrylamide)/Chitosan Semi-IPN

Yating Liu¹, Yunhai Liu^{1,2,3}, Xiaohong Cao^{1,3}, Rong Hua^{1,3}, Youqun Wang¹, Qin Li¹

¹ Chemical, Biological and Materials Sciences Department,

² Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense

³ State Key Laboratory Breeding Base of Nuclear Resources and Environment

East China Institute of Technology

Walton_liu@163.com

Abstract—In this paper, thermo-sensitive semi-IPN (inter-penetrating network) hydrogels were prepared by introducing chitosan (CS) as a metal ion receptor into the poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels with an IPN technique. The swelling behavior of the semi-IPN hydrogels under different temperatures was studied. Feasibility of U (VI) sorption using the prepared hydrogels were investigated at different optimized conditions of contact time, initial concentration of U (VI) and temperature. The kinetic study demonstrated that the pseudo-first-order model correlated with the experimental data better than the pseudo-second-order model examined. To discuss the mechanism of adsorption of uranium (VI) ions on the semi-IPN hydrogels at temperature above and below the lower critical solution temperature (LCST), Langmuir and Freundlich adsorption models were applied to describe the isotherms at 293 and 323 K. The Langmuir model correlates well with the U (VI) adsorption equilibrium data for the concentration range of 5-30 mg/L at lower temperature. The adsorption results at different temperature showed that the PNIPAAm/CS hydrogels adsorbed UO_2^{2+} ions at lower temperature. Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), free energy change (ΔG) were determined. The negative values of ΔH and ΔS indicated that the spontaneous nature and exothermic process of the U (VI) adsorption. The increase in the value of ΔG with a rise in temperature showed that the sorption was more favorable to low temperature.

Keywords—Thermo-sensitive; hydrogel; Inter-Penetrating Networks; Uranium; Adsorption

I. INTRODUCTION

Uranium is one of the most serious contamination concerns because of its radioactivity and toxicity. Uranium released into the environment can eventually reach the top of the food chain and be ingested by humans, causing severe kidney or liver damage [1, 2]. The removal of U (VI) from aqueous waste solutions seems to be a significantly useful subject for environmental control [3] and many techniques have been developed and studied for the removal of uranium from aqueous media, including chemical precipitation [4], filtration [5], ion-exchange [6], solvent extraction [7] and adsorption [8] etc. Among these, adsorption of U (VI) onto various adsorbents is thought to be one of the promising approaches from purification, environmental, and radioactive waste disposal points of view [9, 10]. Hence, environmental engineers and scientists have been trying to find easy, effective, economic, and eco-friendly techniques for removal of uranium from wastewater. A large variety of adsorbents like activated carbon, alga, bentonite, chitosan have been investigated [11-14].

However, the efficiency of an adsorbent is not only determined by sorption characteristics but also by desorption behaviors. Uranium can be desorbed from adsorbents by acid treatment resulting in secondary pollution. Hence, there is intense research focus to develop an adsorbent which can release the absorbed uranium more easily and environment-friendly. In recent years, intelligent (or smart) hydrogels, especially poly (*N*-isopropylacrylamide) (hereinafter referred to as PNIPAAm) hydrogel has emerged as preferable for its unique phase separation behavior upon external temperature changes. PNIPAAm hydrogel is well-known for its discontinuous phase separation near the lower critical solution temperature (LCST) and exhibits a sudden shrinking in volume at a temperature right above the LCST which causes secondary pollution [15]. Owing to this unique property, it has been applied in many fields, such as the controlled drug release [16] and metal ions adsorption [17, 18]. To prepare thermosensitive PNIPAAm-related hydrogels with high adsorption ability for heavy metal ions, many strategies have been investigated. One of the most useful approaches is the formation of inter-penetrating network (IPN) structures, comprising two or more networks, which are fully or partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken [19]. Many researchers have prepared PNIPAAm-related IPN materials to introduce adsorption properties to PNIPAAm networks. *N*-(4-vinyl) benzyl ethylenediamine (Vb-EDA), methacrylic acid (MAA) and polyvinyl alcohol (PVA) reported as functional components were introduced into PNIPAAm hydrogels, the prepared hydrogels showed good adsorption abilities [2, 20, 21]. Lee [22] et al prepared semi-interpenetrating network gels with thermo-sensitivity to draw chitosan into PNIPAAm gel, the gel exhibited pH and temperature-sensitivity behaviors and could slow drug release and diffusion from the gels.

We have recently reported a series of uranium adsorbents based on chitosan-coated attapulgite beads, dead fungal biomass of *Penicillium citrinum*, ion-imprinted chitosan/PVA cross-linked hydrogels and ion-imprinted chitosan resin [23-25]. The results showed that these adsorbents had good adsorption capacity and hold great potential for the uranium removal. In the present study, we proposed a novel PNIPAAm/CS semi-IPN hydrogels by conducting chitosan into PNIPAAm hydrogel using IPN technique. The PNIPAAm/CS semi-IPN hydrogel combines the good adsorption capacity of natural polymer with the thermo-sensitive properties of PNIPAAm hydrogels, exhibiting the feasibility for temperature swing adsorption of

U(VI). To the best of our knowledge, similar work has not yet been reported. The swelling behaviors of the semi-IPN hydrogels were studied and sorption behavior of U(VI) ions were discussed in detail using batch equilibrium methods under varying operating conditions.

II. EXPERIMENTAL

A. Materials and Apparatus

Chitosan (CS) with an average molecular weight of 2.0×10^5 and a degree of deacetylation of 76% was supplied from Sinopharm Chemical Reagent Co., Ltd. N, N'-Methylenebisacrylamide (MBA) as a crosslinker, ammonium persulfate (APS) as the initiator and N, N, N', N'-Tetramethylethylenediamine (TEMED) as the accelerator were purchased from Fuchen Chemical Reagent Co., Ltd. N-isopropylacrylamide (NIPAAm) as the monomer from Aladdin Chemistry Co., Ltd. was further purified by recrystallization from hexane. All other reagents used were of analytical grade and used without further purification.

A U(VI) stock solution was prepared by dissolving 1.1792 g of uranium oxide (U₃O₈) in a 250 mL beaker volumetric flask by adding 10 mL hydrochloric acid ($\rho = 1.18$ g/mL) and 2 mL 30% hydrogen peroxide with continuously heating slowly to near dryness, then dissolving it with 10 mL hydrochloric acid and transferring to a 1000-mL volumetric flask diluted with distilled water to volume to form a U(VI) stock solution with concentration of 1 mg/mL. Concentration of U(VI) solution was determined spectrophotometrically by using arsenazo-III procedure [26].

A JSM-5610LV scanning electron microscope (SEM, Japan) was used to investigate the morphological properties of the biosorbent. Fourier transform infrared (FTIR) spectra of the semi-IPN hydrogels before and after U(VI) adsorption were conducted on a Nicolet 380 FT-IR spectrometer (USA).

B. Preparation of PNIPAAm/CS Semi-IPN Hydrogels

The semi-IPN hydrogels were prepared by free radical copolymerization. Chitosan, as the chelating monomer, was dissolved completely in 2 wt % acetic acid. To this solution, NIPAAm, MBA, APS and TEMED were added, respectively. The concentration of the materials used in the aqueous solution were NIPAAm : MBA : TEMED : APS = 1000 : 30 : 10 : 1 mol/m³. The polymerization was carried out at 10 °C with a reaction time of 12 h under a nitrogen atmosphere. The formed hydrogels were extensively washed with deionized water to remove the unreacted monomers. After that the hydrogels were cut into cubes and were dried in a vacuum freeze drier.

C. Measurement of Swelling Ratio

The dried PNIPAAm/CS semi-IPN hydrogels were immersed in deionized water at different temperatures until swelling equilibrium was attained. The weight of the swollen hydrogels (W_s) was determined after removing the surface water by blotting with filter paper. The weight of the dry sample (W_d) was determined after drying the hydrogels in a vacuum oven for one day. The swelling ratio (SR) was calculated from the following equation:

$$SR = \frac{W_s - W_d}{W_d} \quad (1)$$

D. Adsorption Experiments

Adsorption experiments were carried out by the batch technique in a reciprocating thermostated air bath shaker. A concussion agitation speed of 200 rpm was adopted for all experiments. In a typical batch adsorption experiment, 0.05 grams of dry hydrogels were suspended in 50 mL solution of U(VI). The adsorption of U(VI) was studied as a function of contact time, initial concentration and temperature. The initial pH of the solution was adjusting using 0.1 mol/L HCl and 0.1 mol/L NaOH.

The amount of U(VI) adsorbed per unit mass of adsorbent at equilibrium, q_e was calculated using the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where C_o and C_e are the initial and equilibrium liquid-phase U(VI) concentrations (mg/L) respectively, V is the liquid-phase volume (mL) and W is the mass of adsorbent (g).

III. RESULT AND DISCUSSION

A. Characterization of Hydrogels

The scanning electron microscopy (SEM) image of the prepared PNIPAAm/CS semi-IPN hydrogels microstructure was shown in Fig. 1 at 5000 \times magnification. It was found that the surfaces of the PNIPAAm/CS semi-IPN hydrogels generally had a threedimensional network. The network structure of the hydrogels was important from the viewpoint of their application due to supplying very suitable places for the sorption of uranium ions.

Fig. 2 shows the FTIR spectra of the semi-IPN PNIPAAm/CS hydrogels before and after U(VI) adsorption. As shown in Fig. 2, a characteristic strong and broad band appeared at around 3300 ~ 3400 cm⁻¹; corresponding to the stretching vibration of -OH group in CS and -NH group in PNIPAAm. The band at 2971 cm⁻¹, 2928 cm⁻¹ should be related to the -CH₃ and -CH groups. Two important absorption bands are verified at the frequency of 1652, 1542 cm⁻¹, and these vibration bands are mostly attributed to amide I, amide II groups in the chain of PNIPAAm. And the band located at 1458 cm⁻¹ is characteristic of -CH₃ asymmetrical bending vibration. For PNIPAAm/CS semi-IPN hydrogels, the adsorption band of two -CH₃ groups in the isopropyl group located at 1387, 1368 cm⁻¹. A peak at 1082 cm⁻¹ is also observed, which may be related to the secondary amine bonds -NH. After U(VI) adsorbed onto the PNIPAAm/CS semi-IPN hydrogels, compared to the spectrum of the hydrogels before U(VI) adsorption, a new peak appearing at 909 cm⁻¹ which belonged to the stretching vibrations of uranyl ions. At the same time, the peak intensity at 1458, 1171 cm⁻¹ attributed to -CH₃ and -C-C strengthened, while the spectrum showed a decrease in the absorption intensity of -NH and -OH vibration around 3300 cm⁻¹, this was due to the low number of -OH present on the polymer chain after the uranium adsorption had taken place. All the above characterization data show that we synthesized the hydrogels adsorbed uranium ions successfully.

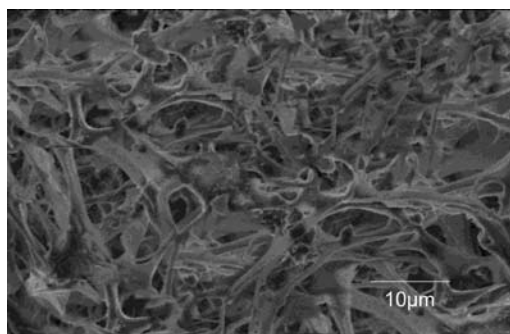


Fig. 1 SEM image of PNIPAAm/CS semi-IPN hydrogels

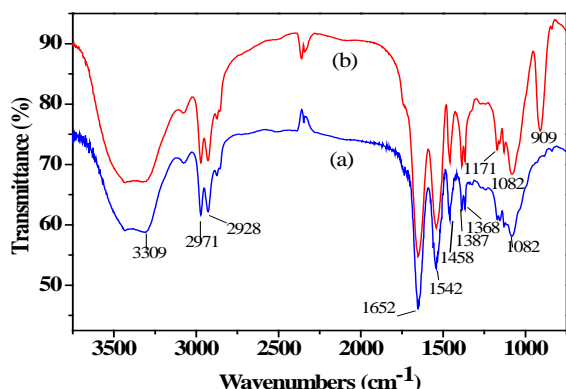


Fig. 2 FTIR spectra for PNIPAAm/CS semi-IPN hydrogels before (a) and after (b) U(VI) adsorption

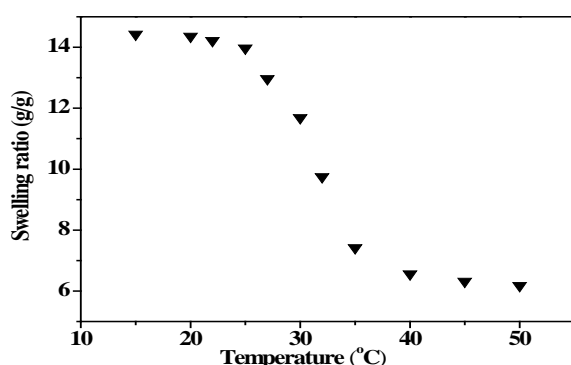


Fig. 3 Swelling ratio of PNIPAAm/CS semi-IPN hydrogels in water as a function of temperature

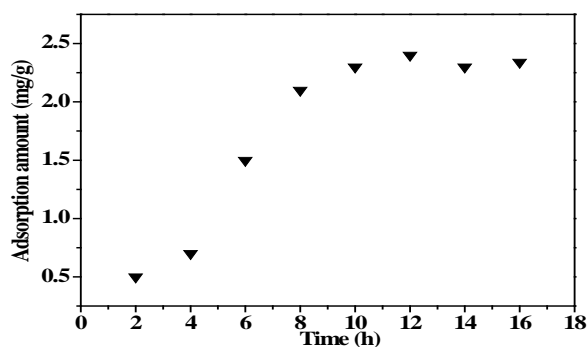


Fig. 4 Adsorption of U(VI) on PNIPAAm/CS semi-IPN hydrogels as a function of contact time (U(VI): 20 mg/L; PNIPAAm/CS: 0.05 g; pH: 5; T: 303 K; t: 10 h; V: 50 mL).

B. Effect of Temperature on Swelling Ratio

The temperature sensitivity of the equilibrium swelling ratio of the PNIPAAm/CS semi-IPN hydrogel was examined to determine their temperature dependence of the swelling and collapse processes. As shown in Fig. 3, the PNIPAAm/CS semi-IPN hydrogel had significant changes in swelling ratio at 35°C. It is well known that the NIPAAm molecule contains a hydrophilic group (amido-, -CONH-) and a hydrophobic group (isopropyl-, -CH(CH₃)₂). The hydrophilic group in the polymer structure will form an intermolecular hydrogen bond with the surrounding water at temperature below the hydrogel volume phase transition temperature and water penetrating into the PNIPAAm/chitosan semi-IPN hydrogel is in a bound state at the low temperature. During the increase of temperature, hydrophobic interactions of the isopropyl group of PNIPAAm increases and the hydrophilic group in the NIPAAm will be turned into an intramolecular hydrogen bond. These two results make the water molecule inside the hydrogel change from a bound state to a free state and the hydrogel precipitate from aqueous solution. Consequently, the swelling ratios of the PNIPAAm/CS semi-IPN decreased rapidly above the hydrogel transition temperature.

C. Effect of Contact Time on Adsorption Of U(VI)

Effect of contact time on the adsorption of uranium(VI) on PNIPAAm/CS semi-IPN hydrogel is illustrated in Fig. 4. It is known that adsorption process could be dependent on and controlled with different kinds of mechanisms. In order to clarify the mechanism of sorption kinetics, three adsorption models were applied to evaluate the experimental data, including Lagergren's pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle diffusion mode were used.

The pseudo-first-order model of Lagergren is given as[27]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where k_2 (g/(mg h)) is the rate constant of pseudo-second-order adsorption. Plotting the t/q_t against t , a line can be obtained and the q_e also can be calculated.

The intraparticle diffusion model can be described as[28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 (g/(mg h)) is the rate constant of pseudo-second-order adsorption.

Intra-particle diffusion model is given as:

$$q_t = k_t t^{1/2} + C \quad (5)$$

Where k_t denote the adsorption rate constant of intra-particle diffusion model (mg/g min^{-1/2}) and is the slope of straight-line portions of the plot of q_t vs. $t^{0.5}$. C is the maximum adsorption capacity (mg/g).

The calculated results of the pseudo-first-order, pseudo-second-order and intra-particle diffusion model constants are given in Table 1.

As shown in Table 1, the linear relationships obtained ($R^2 > 0.9$) in the case of the first-order kinetic model was closer to the experimental values compared to those calculated by the second-order kinetic model and the intra-particle diffusion model. Hence, it could be made the conclusion that the adsorption of U(VI) ion on semi-IPN PNIPAAm/CS hydrogels

well followed as the first order kinetic model. It was similar to other chemical reactions that the pseudo-first-order adsorption was the common adsorption type. The R² values indicated that the data could be well described by adsorption equation and show the first-order nature of the process between solutions and adsorbent. The pseudo-first order kinetic model has been used for reversible reaction with an equilibrium being established between liquid and solid phases [29].

TABLE I
KINETIC PARAMETERS FOR THE ADSORPTION OF U(VI) ON PNIPAAm/CS SEMI-IPN HYDROGELS

Pseudo-first-order	Pseudo-second-order	Intraparticle diffusion model
		$k_t=0.8167 \text{ mg g}^{-1} \text{ min}^{-1/2}$
$k_1=0.6186 \text{ h}^{-1}$	$k_2=0.1503 \text{ g mg}^{-1} \text{ h}^{-1}$	$C=-0.5866 \text{ mg g}^{-1}$
$R^2=0.9013$	$R^2=0.3311$	$R^2=0.8520$

D. Effect of Initial U(VI) Concentration and Sorption Isotherms

The effect of initial uranium concentration was studied by using a range of initial uranium concentrations (5, 10, 15, 20, 25 and 30 mg/L) at two fixed temperatures (293 and 323 K). As shown in Fig. 5, the U(VI) uptake capacity increases from 1.55 to 2.59 mg/g when the initial uranium concentration goes up from 5 to 30 mg/L. This might be due to higher metal ion concentration enhancing the driving force to overcome mass transfer resistance between the aqueous and solid phases. Such a slow adsorption was considered since the shrinkage of the thermosensitive gel network and the formation of the dense part of the network. Further, it is observed that the adsorption of uranium by PNIPAAm/CS semi-IPN hydrogels decreased with an increase in temperature indicating that the process to be exothermic in nature.

The equilibrium data were evaluated according to the Langmuir and Freundlich isotherms. The Langmuir isotherm model is the simplest theoretical model for monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption. Linearized form of the Langmuir equation is given as [30]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \quad (6)$$

where C_e is the equilibrium concentration (mg/g), q_e is the amount of U(VI) adsorbed at equilibrium (mg/g), Q_m is the saturated monolayer adsorption (mg/g), b is the Langmuir constant related to the affinity of binding sites and is a measure of the energy of adsorption (mL/mg).

The Freundlich isotherm model assumes a heterogeneous energetic distribution of the active sites on the adsorbate surface and is tested in the following linearized form [31]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

Where K_F is the adsorption capacity (mg/g) and $1/n$ is the Freundlich constant indicating adsorption intensity. K_F and

$1/n$ can be evaluated from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$, respectively.

In order to assess the effect of temperature between temperature lower and higher than then the LCST on the adsorption of uranium(VI), the experimental data fitted by both Langmuir and

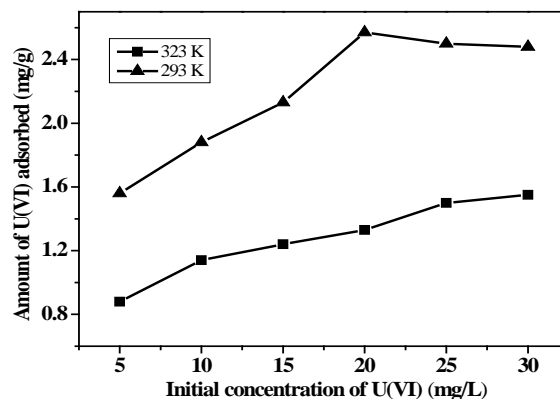


Fig. 5 U(VI) adsorption onto PNIPAAm/CS semi-IPN hydrogels as a function of initial concentration of U(VI) solutions at 293 K (▲) and 323 K (■) (PNIPAAm/CS: 0.05 g; pH: 5; T: 303 K; t: 10 h; V: 50 mL).

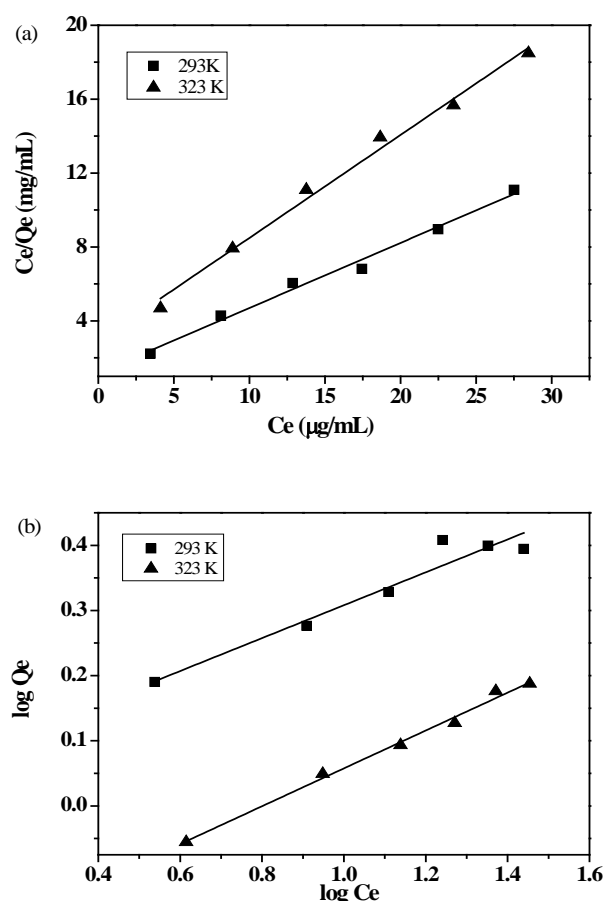


Fig. 6 Adsorption isotherm of U(VI) on the PNIPAAm/CS semi-IPN hydrogels at 293 K (■) and 323 K (▲), linearized according to (a) Langmuir, (b) Freundlich equations.

TABLE II
ISOTHERM PARAMETERS OF U(VI) ADSORPTION ON PNIPAAm/CS SEMI-IPN HYDROGELS

temperature(K)	Langmuir isotherm			Freundlich isotherm		
	Q_m (mg/g)	b (L/g)	R^2	1/n	k_F (mg/g)	R^2
293	2.86	0.29	0.9868	0.25	1.14	0.9239
323	1.79	0.19	0.9822	0.29	1.71	0.9918

TABLE III
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF U(VI) ON SEMI-IPN HYDROGELS

ΔH (kJ mol)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)					
		283K	293K	303K	313K	323K	333K
-9.64	-0.0008	-9.41	-9.40	-9.39	-9.38	-9.38	-9.37

Freundlich isotherms at the two temperatures (lower and higher than the LCST) were obtained and tabulated in Table 2. From Table 2, the max adsorption capacity (Q_m) was found to decrease with rising temperature, revealing the exothermic nature of the ongoing process and the value of b represents the enthalpy of sorption which should vary with temperature. At 323 K (above the LCST), the Freundlich equation fitted better than the Langmuir equations judging from the higher R^2 value (0.9918). And the R^2 values for the Langmuir and Freundlich models were 0.9868 and 0.9239 at 293 K, respectively, indicating that the Langmuir model could well correlate the experiment data at lower temperature. It might be explained that at the lower temperature, the adsorption of U(VI) took place preferably forming a monolayer sorption on to the surface of the PNIPAAm/CS semi-IPN hydrogels with a finite number of identical site. And when the temperature went higher than the LCST, the uptake of U(VI) occurred on a heterogeneous surface by multi-layer adsorption due to the shrinkage of the hydrogels.

E. Temperature-Dependent Adsorption of U(VI) Ions in Aqueous Solutions

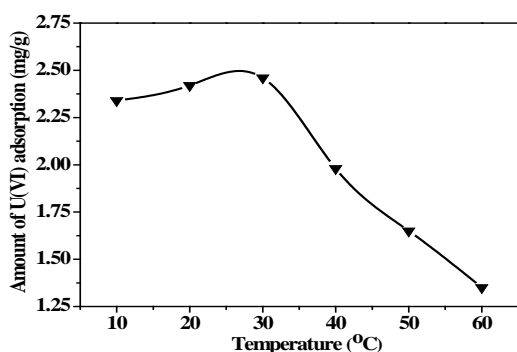


Fig. 7 Effect of temperature on U(VI) adsorption (U(VI): 20 mg/L; PNIPAAm/CS: 0.05 g; pH: 5; t: 10 h; V: 50 mL).

Effect of environmental temperature on the adsorption characteristic of PNIPAAm/CS semi-IPN hydrogels toward uranyl ions in aqueous solutions was shown in Fig. 7. The hydrogels had better and higher adsorption abilities at the low temperature. There is a slight decrease of U(VI) adsorbed on the hydrogels upon the temperature increased. This was mainly depended on the physical adsorption and the chelating groups in the networks, in which, the chitosan groups in

PNIPAAm/CS semi-IPN hydrogels perhaps played a more important role in binding uranyl ions. The hydrogens of U(VI) adsorption under the temperature lower and higher than the LCST was illustrated in Fig. 8, the prepared hydrogels were confirmed to exhibit an interesting behavior as that U(VI) ions adsorbed at lower temperature and desorbed at higher temperature. As the temperature increase, the volume and the adsorption area for chitosan decrease, which might reduce the adsorption of uranyl ions, it seemed U(VI) ions had been “forced out” of the semi-IPN networks

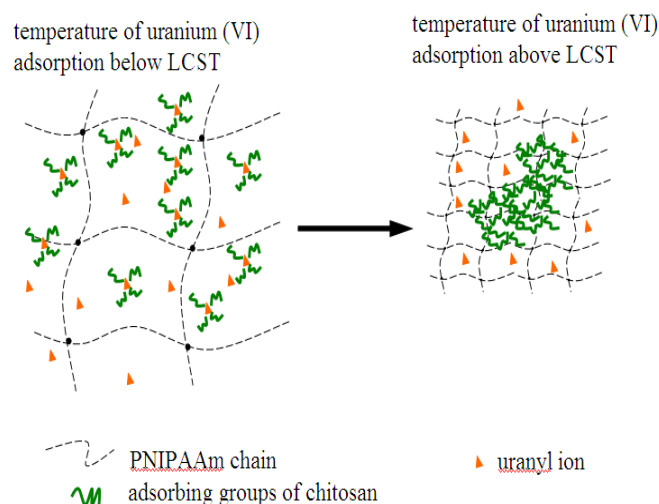


Fig. 8 Schematic diagram of thermo-sensitive PNIPAAm/CS semi-IPN hydrogels of U(VI) adsorption under the temperature lower and higher than the LCST

Consequently, at temperature lower than the LCST, the networks stretched, which made it easier for the cavities of chelating groups to capture the guest ions, so that the PNIPAAm/CS semi-IPN hydrogels exhibited a higher adsorption capacity. Therefore, the developed PNIPAAm/CS semi-IPN hydrogels were thermo-sensitive smart adsorbent materials which could easily release the adsorbed substance by simply increasing the environmental temperature.

F. Thermodynamic of U(VI) Adsorption

The thermodynamic parameters of the adsorption process were obtained from experiments at various temperatures (283, 293, 303, 313, 323, 333K) using the following equations [32, 33]:

$$K_d = \frac{V}{m} \left(\frac{C_0}{C_e} - 1 \right) \quad (8)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

Where K_d is the distribution coefficient (L/g), C_0 is the initial concentration of uranium solution (mg/L), C_e is the equilibrium concentration of uranium solution (mg/L), V is the volume of solution (mL), m is the mass of adsorbents (g), T is temperature (K) and R is the gas constant (8.314 J·mol⁻¹·K⁻¹).

The values of ΔH and ΔS were obtained from the slope and intercept of $\ln K_d$ versus $1/T$. The values of the thermodynamic parameters for U(VI) sorption on semi-IPN hydrogels are given in Table 3.

The negative values of enthalpy change, ΔH , suggested the exothermic nature of adsorption of U(VI) ions on PNIPAAm/CS semi-IPN hydrogels, while the negative values of ΔS reflected the affinity of the hydrogels for U(VI) and confirmed the decreased randomness at the solid solution interface during adsorption. As shown in table 3,

the numerical value of ΔG increase with an increase in temperature, indicating that the reaction is more favorable to lower temperatures. In addition, the negative free energy (ΔG) indicated that the adsorption onto the hydrogels was a feasible and spontaneous process.

IV. CONCLUSIONS

In this study, the PNIPAAm/CS semi-IPN hydrogels synthesized by inter-penetrating polymer network technique with N-isopropylacrylamide and chitosan had been used to investigate the adsorption of U(VI) ions in aqueous solution. The hydrogels exhibit good thermosensitive and U(VI) adsorption characteristics. The amount of U(VI) ions adsorbed on the semi-IPN gels decreases with temperature in the range of 10-60 °C, corresponding to the drastic change in the swelling ratio of the gels due to the hydrophilic/hydrophobic transition. The kinetic study demonstrated that the pseudo-first-order model correlated with the experimental data better than the pseudo-second-order model examined. And Langmuir model is applied to describe the adsorption process, the adsorption capacity calculated from the Langmuir isotherm equation for uranium ions was 4.04 mg/g. Various thermodynamics parameters, such as ΔG , ΔH , ΔS , were calculated from the data, the thermodynamics of U(VI) indicates spontaneous and exothermic nature of process.

ACKNOWLEDGMENT

We gratefully acknowledge the financial support provided by National Natural Science Foundation of China (Grant No. 21101024), Key Project of Chinese Ministry of Education (Grant No. 211086), Project of Jiangxi Provincial Department of Education (Grant No. GJJ10493) and China Postdoctoral Science Foundation (Grant No. 20110490857).

REFERENCES

- [1] S. Xie, J. Yang, C. Chen, X. Zhang, Q. Wang and C. Zhang, "Study on biosorption kinetics and thermodynamics of uranium by *Citrobacter freundii*," J. Environ. Radioactiv., vol. 99, pp. 126-133, Nov. 2008.
- [2] Alvarez-Lorenzo, O. Guney, T. Oya, Y. Sakai, M. Kobayashi, T. Enoki, Y. Takeoka, T. Ishibashi, K. Kuroda, K. Tanaka, G. Wang, A. Y. Grosberg, S. Masamune and T. Tanaka, "Reversible adsorption of calcium ions by imprinted temperature sensitive gels," J. Chem. Phys., vol. 114, pp. 2812-2816, Nov. 2001.
- [3] T. Tsuruta, "Bioaccumulation of uranium and thorium from the solution containing both elements using various microorganisms," J. Alloys Compd., vol. 408-412, pp. 1312-1315, Nov. 2006.
- [4] Krestou, A. Xenidis and D. Papias, "Mechanism of aqueous uranium(VI) uptake by hydroxyapatite," Miner. Eng., vol. 17, pp. 373-381, Nov. 2004.
- [5] N. Kim, D. B. Shon, H. Park, W. K. Choi and K. W. Lee, "The Development of Precipitation-Filtering Technology for Uranium Electrokinetic Leachate," Sep. Purif. Technol., vol. 79, pp. 144-150, Nov. 2011.
- [6] Aziz, S. Jan, F. Waqar, B. Mohammad, M. Hakim and W. Yawar, "Selective ion exchange separation of uranium from concomitant impurities in uranium materials and subsequent determination of the impurities by ICP-OES," J. Radioanal. Nucl. Chem., vol. 284, pp. 117-121, Nov. 2010.
- [7] Y. Zhao, C. Liu, M. Feng, Z. Chen, S. Li, G. Tian, L. Wang and J. Huang, "Solid phase extraction of uranium (VI) onto benzoylthiourea-anchored activated carbon," J. Hazard. Mater., vol. 176, pp. 119-124, Nov. 2010.
- [8] L. Zhang, Y. Sun, M. Luo, S. Liu and J. Hu, "Adsorption of uranium by chemically modified titanate nanowhiskers," Acta Materialia Compositae Sinica., vol. 28, pp. 96-102, Nov. 2011.
- [9] Mellah, A. Silem, A. Boualia and R. Kada, "Adsorption of organic matter from a wet phosphoric acid using activated carbon: equilibrium study," Chem. Eng. Process., vol. 31, pp. 191-194, Nov. 1992.
- [10] M. Saleem, M. Afzal, R. Qadeer and J. Hanif, "Selective adsorption of uranium on activated charcoal from electrolytic aqueous solutions," Sep. Sci. Technol., vol. 27, pp. 239-253, Nov. 1992.
- [11] Tian, J. Geng, Y. Jin, C. Wang, S. Li, Z. Chen, H. Wang and Y. Zhao, "Sorption of uranium (VI) using oxime-grafted ordered mesoporous carbon CMK-5," J. Hazard. Mater., vol. 190, pp. 442-250, Nov. 2011.
- [12] M. Ghasemi, A. R. Keshtkar, R. Dabbagh and S. JaberSafdari, "Biosorption of uranium (VI) from aqueous solutions by Ca-pretreated *Cystoseira indica* alga: breakthrough curves studies and modeling," J. Hazard. Mater., vol. 189, pp. 141-149, Nov. 2011.
- [13] S. Aytas, M. Yurtlu and R. Donat, "Adsorption characteristic of U (VI) ion onto thermally activated bentonite," J. Hazard. Mater., vol. 172, pp. 667-674, Nov. 2009.
- [14] Wang, J. Liu, X. Wang, Z. Xie and N. Deng, "Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan," J. Hazard. Mater., vol. 168, pp. 1053-1058, Nov. 2009.
- [15] S. Hirotsu, Y. Hirokawa and T. Tanaka, "Volume-phase transitions of ionized N-isopropylacrylamide gels," J. Chem. Phys., vol. 87, pp. 1392-1395, Nov. 1987.
- [16] X. Z. Zhang, D. Q. Wu and C. C. Chu, "Synthesis, characterization and controlled drug release of thermosensitive IPN-PNIPAAm hydrogels," Biomaterials, vol. 25, pp. 3793-3805, Nov. 2004.
- [17] Tokuyama, T. Iwama, "Solid-phase extraction of indium(III) ions onto thermosensitive poly(N-isopropylacrylamide)," Sep. Purif. Technol., vol. 68, pp. 417-421, Nov. 2009.
- [18] Tokuyama, A. Kanehara, "Temperature swing adsorption of gold(III) ions on poly(N-isopropylacrylamide) gel," React. Funct. Polym., vol. 67, pp. 136-143, Nov. 2007.
- [19] IUPAC Compendium of Chemical Terminology 2nd, pp. 2005-2005, Nov. 1997.
- [20] R. Kanazawa, T. Yoshida, T. Gotoh and S. Sakohara, "Preparation of Molecular Imprinted Thermosensitive Gel Adsorbents and Adsorption/Desorption Properties of Heavy Metal Ions by Temperature Swing," J. Chem. Eng. Jpn., vol. 37, pp. 59-66, Nov. 2004.
- [21] Zhang, R. Bhat, K. D. Jandt, Temperature-sensitive PVA/PNIPAAm semi-IPN hydrogels with enhanced responsive properties, Acta Biomaterialia, vol. 5, pp. 488-497, Nov. 2009.
- [22] W. Lee, Y. Chen, Studies on preparation and swelling properties of the N-isopropylacrylamide/chitosan semi-IPN and IPN hydrogels, J. Appl. Polym. Sci., vol. 82, pp. 2487-2496, Nov. 2001.
- [23] Pang, Y. Liu, X. Cao, R. Hua, C. Wang and C. Li, "Adsorptive removal of uranium from aqueous solution using Chitosan-coated attapulgite," J. Radioanal Nucl Chem., vol. 286, pp. 185-193, Nov. 2010.
- [24] Pang, Y. H. Liu, X. H. Cao, M. Li, G. L. Huang, R. Hua, C. X. Wang, Y. T. Liu and X. F. An, "Biosorption of uranium (VI) from aqueous

- solution by dead fungal biomass of *Penicillium citrinum*,” *Chem. Eng. J.*, vol. 170, pp. 1-6, Nov. 2010.
- [25] Y. Liu, X. Cao, Z. Le, M. Luo, W. Xu and G. Huang, “Pre-concentration and determination of trace uranium (VI) in environments using ion-imprinted chitosan resin via solid phase extraction,” *J. Brazil Chem. Soc.*, vol. 21, pp. 533-540, Nov. 2010.
- [26] T. M. Bhatti, A. Mateen, M. Amin, K. A. Malik and A. M. Khalid, “Spectrophotometric determination of uranium (VI) in bacterial leach liquors using arsenazo III,” *J. Chem. Technol. Biotechnol.*, vol. 52, pp. 331-341, Nov. 1991.
- [27] S. Lagergren, “Zur theorie der sogenannten adsorption gelöster stoffe,” *Kungliga Svenska Vetenskapsakademiens Handlingar*, vol. 24, pp. 1-39, Nov. 1898.
- [28] W. Weber, J. Morris, “Intraparticle diffusion during the sorption of surfactants onto activated carbon,” *J. Sanit Eng Div Am Soc Civ Eng.*, vol. 89, pp. 53-61, Nov. 1963.
- [29] S. Low, C. K. Lee and S. C. Liew, “Sorption of cadmium and lead from aqueous solutions by spent grain, *Process Biochem.*, vol. 36, pp. 59-64, Nov. 2000.
- [30] Langmuir, “The constitution and fundamental properties of solids and liquids,” *J. Am. Chem. Soc.*, vol. 38, pp. 2221-2295, Nov. 1916.
- [31] M. F. Freundlich, “Über die adsorption in lasungen,” *Z. Phys. Chem.*, vol. 57, pp. 385-470, Nov. 1906.